



Hydrogen peroxide production by water electrolysis: Application to disinfection

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Abstract

Hydrogen peroxide was produced by direct current electrolysis using only two electrodes, a carbon felt cathode and a RuO₂ coated titanium anode. The required oxygen was supplied by oxidation of water and by transfer from the atmosphere or by pure oxygen injection. The current was maintained below a maximum value to avoid peroxide reduction. A high peroxide production rate was reached and a 15 mg l⁻¹ concentration was maintained. The electrolysis removed turbidity and dissolved organic carbonaceous compounds from municipal sewage plant effluents. Real effluents were significantly disinfected owing to the direct effect of electric current and the indirect effect of peroxide. A residual effect was also observed.

1. Introduction

Hydrogen peroxide is a metastable molecule of high (1.77 V) redox potential. Its disinfecting properties result from direct molecular action [1] and, more importantly, from free radicals formed by catalytic reactions [2]. Hydrogen peroxide can be chemically produced from peroxigenated compounds or by the electrolysis of sulphuric acid or sulphates at a platinum anode [3]. A conventional electrochemical technique uses the cathodic reduction of oxygen with potassium hydroxide as the electrolyte [4]. Recent work has described peroxide production in a three-electrode cell with the addition of Fenton reagent [5]. McIntyre proposed electroreduction of oxygen in alkaline solutions with a two-electrode cell [6]. However, the challenge consists in producing hydrogen peroxide, by water electrolysis, in a two-electrode cell without chemical addition.

Moreover, conventional techniques of water disinfection are often inconvenient. Chlorination generates hazardous and carcinogenic compounds [7]. Ozone and ultraviolet light, though efficient and producing harmless derivatives, prove to be expensive [8]; moreover ultraviolet light has no residual effect like chlorine or ozone. Research on alternative oxidants is required to identify inexpensive techniques that produce harmless substances and induce a residual effect. Hydrogen peroxide produced in a two-electrode cell could be the basis for an efficient and economical water disinfection process.

This work describes the design and testing of a two-electrode cell. Suitable electrodes are identified and the

production of peroxide and its oxidative properties are studied.

2. Material and methods

2.1. Preliminary voltametric study

A preliminary voltametric study was carried out with a three-electrode Voltalab 21 system (Radiometer Analytical) equipped with a rotating working electrode. It included a potentiostat/galvanostat (Tacussel 20 V/1A PGP 201). The reference electrode was a saturated calomel (Hg/Hg₂Cl₂/KCl) electrode (Tacussel XM 110), while the auxiliary electrode was platinum (Tacussel Pt XM 140). The materials tested as cathode were platinum, zinc, zirconium, copper, graphite and vitreous carbon. For the anode, the tested materials were platinised titanium, RuO₂ coated titanium and vitreous carbon.

2.2. Peroxide production

The cylindrical PVC electrolysis cell had two electrodes separated by an insulating diaphragm (Figure 1). The electrodes were made from suitable materials identified in the preliminary study (vitreous carbon for the cathode and DSA for the anode). The 177 cm² area carbon felt cathode (RVC 4000, Le Carbone Lorraine) of 0.94 porosity gave low hydraulic resistance. A steel grid on the carbon felt provided electric contact. The DSA anode had a solid surface area of 67 cm² and a

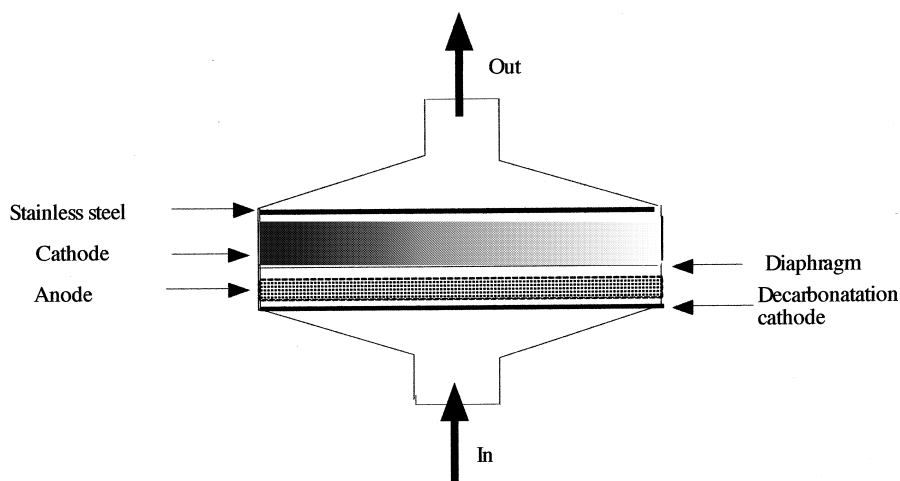


Fig. 1. Electrolysis cell.

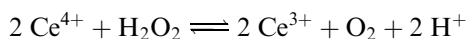
void area of 110 cm². A stainless steel grid cathode enabled polarisation of the carbon electrode to ensure the elimination of carbonate deposits when required. A brass grid, used to catalyse the formation of free radicals [1], was installed over the steel grid during the disinfection runs.

Two experimental units were operated. Unit 1 included a stirred 5 litre tank in a closed loop with the electrolysis cell in which a recycling pump induced perfect mixing of the liquid phase. The mechanical stirring induced oxygen transfer from the atmosphere to the liquid phase. In unit 2, pure oxygen was injected into the loop after removal of the stirred tank (no reservoir). The liquid phase was tap water in all the peroxide production experiments.

Noncarbonated natural mineral water was contaminated with the effluent of a municipal wastewater treatment plant including a biological process (Montpellier or Mèze, France). Some experiments were carried out with a pure culture of *Pseudomonas aeruginosa* containing 20 000 cells ml⁻¹.

2.3. Analytical techniques

Hydrogen peroxide concentrations were determined by cerium sulphate oxidation of peroxide using ferrous orthophenanthroline as indicator [1].

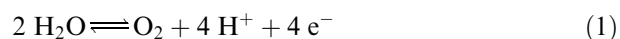


Oxygen concentrations were given by a WTW-SL 340 oxymeter. Dissolved organic carbon (DOC) was measured with a TOC meter Shimadzu TOC 5000. Turbidity was obtained with a Hach DR 2000 turbidimeter. 254 nm absorbance was measured with a Jasco V-530 spectrophotometer. Most other parameters, particularly microorganism concentration and chemical oxygen demand (COD), were determined in conformity with Standard Methods [9].

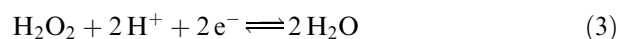
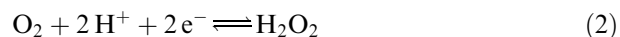
3. Results and discussion

3.1. Preliminary voltametric study

Water oxidation takes place on the anode:



For most cathode materials, dissolved oxygen reduction occurs in one step whereas a vitreous carbon cathode induces a two-step process. Two successive waves of oxygen reduction were observed (Figure 2). Addition of hydrogen peroxide to tap water enabled to establish that the second wave corresponds to peroxide reduction. This result is consistent with the following mechanism:



A dimensionally stable anode was selected since it limits the oxidation of peroxide produced at the cathode. The decomposition potentials of water and peroxide are

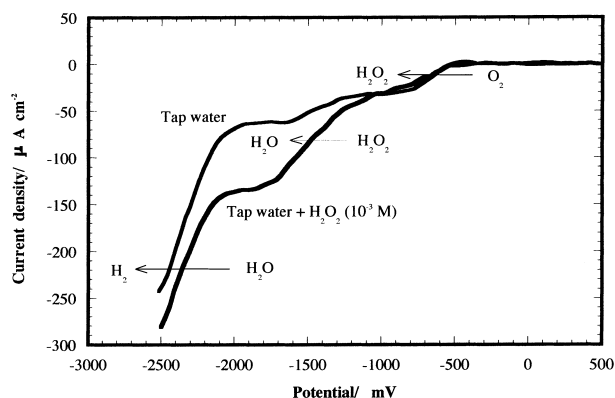


Fig. 2. Oxygen reduction in tap water and in hydrogen peroxide solution (10⁻³ M) at a vitreous carbon rotating cathode (1000 rpm).

identical (1 V) (Figure 3). Water being in excess, the peroxide oxidation was limited by mass transport.

Reaction 3 should be limited to ensure peroxide production. A third electrode and a potentiostat, generally expensive, are not required if the electronic balance favours Reaction 2. Four electrons are produced on the anode. Two electrons are used to reduce the transferred oxygen, whereas the other two should exclusively reduce the oxygen produced on the anode. This condition is met if the current, I , is less than a maximum value given by:

$$I \leq \frac{QFC}{M} \quad (4)$$

where Q is the flow-rate through the cell, F the faradayic constant, M the molar mass of oxygen and C the oxygen concentration.

3.2. Hydrogen peroxide production

With no addition of other chemicals to tap water, the peroxide concentration, C_p , linearly increased with elapsed time t . The gradient K_1 depended on the current and the available oxygen concentration, that is, the rate was significantly higher when pure oxygen was injected (Table 1):

$$C_p = K_1 t \quad (5)$$

No plateau was observed. However, in longer runs, a limiting value should be observed as a result of the electrochemical decomposition of peroxide [10]. The rate of peroxide production was proportional to current intensity when there was no limitation by oxygen supply; otherwise the rate reached a plateau (Figure 4). In all cases, the rate is high enough to disinfect water. The electrolytic production of peroxide will be termed electroperoxidation.

The theoretical peroxide concentration is given by

$$C_p = \frac{IM}{2FV} t \quad (6)$$

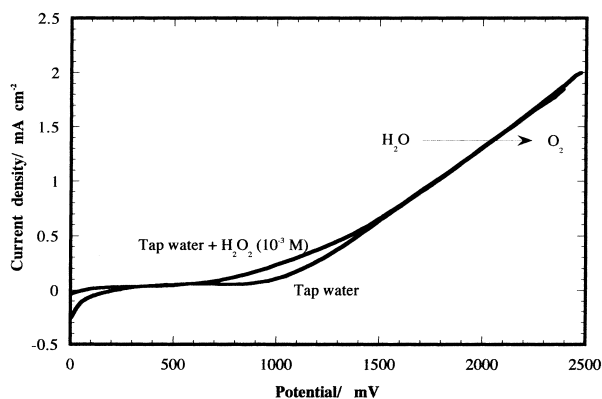


Fig. 3. Water and hydrogen peroxide (10^{-3} M) oxidation at a rotating DSA anode (1000 rpm).

Table 1. Hydrogen peroxide production rate/mg dm $^{-3}$ min $^{-1}$ (determination coefficient between brackets)

Current/A	0.2	0.5	1	2
Unit 1		0.13 (0.98)	0.15 (0.96)	0.18 (0.95)
Unit 2	0.08 (0.98)	0.18 (0.99)	0.33 (0.99)	0.60 (0.99)

where is V the liquid volume. The ratio between the specific production rate, that is, the straight-line slope obtained with unit 2 (Figure 4), and $IM/2FV$ is the faradayic yield whose value was 0.21 ± 0.03 . The limit of the diffusion current, corresponding to the reduction of oxygen into peroxide, was lower than the imposed current. The overall reaction was then limited by diffusion and a small fraction of the overall energy was used to reduce oxygen into peroxide. Moreover, the faradayic yield is low compared to other electrochemical processes; for example, 0.8 was obtained with an electrochemical water softener [11]. Parasitic reactions probably take place, such as oxygen reduction in water, peroxide reduction or peroxide decomposition [10].

Berl [4] and McIntyre [6] studied electroreduction of oxygen in alkaline solution in a two-electrode cell. McIntyre's synthesis was based on the oxidation of sodium hydroxide into oxygen at an anode, whereas hydrogen peroxide was produced via the subsequent reduction of oxygen. Berl [4] carried out similar experiments with potassium salts as the electrolyte. Both authors obtained a 0.9 current efficiency that is quite higher compared to the 0.21 yield obtained in electroperoxidation. This significant difference is probably due to the high electrical resistance of the electroperoxidation cell in which no chemical was added. For example, McIntyre operated at a 2 V potential with a current of 5000 A, whereas the electroperoxidation potential was approximately 25 V with a 2 A current. An electrolyte solution minimises the ohmic loss.

The proportionality between the peroxide production rate and the current agrees with results obtained by Kraft et al. [12], who produced active chlorine by electrolysis of a 150 mg dm $^{-3}$ chloride solution (anode in IrO $_2$) at a rate proportional to the current. The

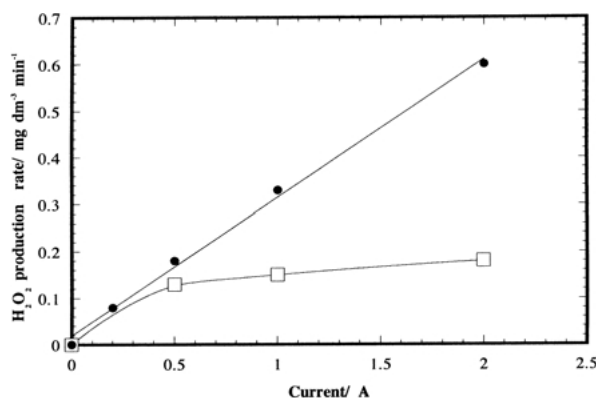


Fig. 4. Hydrogen peroxide production rate against intensity. Key: (□) unit 1; (●) unit 2.

current efficiency was 0.415, twice the electroperoxidation faradaic yield. However, electroperoxidation has many advantages; for example, hydrogen peroxide does not induce offensive byproducts contrary to chlorine.

In the following study concerning the application to water treatment, unit 1 was operated exclusively since it is more convenient and cheaper to operate.

3.3. Application to water treatment

Turbidity takes into account solid and colloidal particles (humic substances, fulvic acids, proteins and microorganisms larger than $0.1\ \mu\text{m}$). Disinfection is hampered by high turbidity [13, 14]. The turbidity contained in the effluent of a municipal wastewater treatment plant was nearly totally removed by electroperoxidation (Figure 5); the initial brown colour disappeared and water became transparent. Electroperoxidation could simultaneously reduce dissolved organic carbon and 254 nm absorbance (Figure 6). The 254 nm absorbance is linked to organic compounds with one or many double bonds.

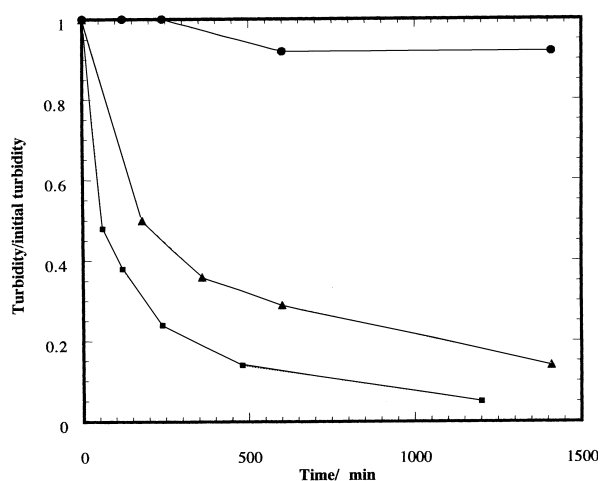


Fig. 5. Turbidity removal (effluent of Montpellier sewage plant; 12 FTU initial turbidity). Key: (●) 0 A; (▲) 1 A; (■) 2.5 A.

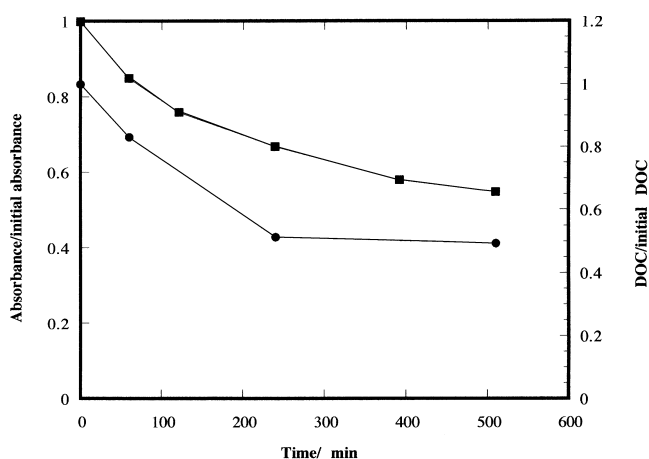


Fig. 6. DOC and 254 nm absorbance removal (effluent of Mèze sewage plant; $40\ \text{mg l}^{-1}$ initial DOC). Key: (■) absorbance; (●) DOC.

Electroperoxidation broke the double bonds producing smaller molecules. Organic pollutants were indeed subjected to two effects: direct anodic oxidation, where the organics are destroyed at the electrode surface, and indirect oxidation where a mediator is electrochemically generated to carry out the oxidation [15]. According to Comninellis [16], two different paths can be followed in anodic oxidation: electrochemical conversion or electrochemical combustion. Electrochemical conversion only transforms the nonbiodegradable organic pollutants into biodegradable compounds. In electroperoxidation, the electrochemical conversion breaks the double bonds producing smaller molecules (Figure 6). Electrochemical combustion yields water and carbon dioxide and no further treatment is then required. The accumulation of OH° radicals favours the combustion reaction. Electrochemical combustion could be responsible for the decrease in the dissolved organic carbon concentration (Figure 6). Indirect oxidation needs the presence of a mediator such as H_2O_2 . Thus, an electron-transfer agent such as $\text{O}_2/\text{H}_2\text{O}_2$ eliminates the organic pollutants.

The oxidation of dissolved organic carbon was incomplete because of refractory compounds or insufficient peroxide production. 40% of the dissolved organic carbon could only be removed, which is low compared to the 80 and 100% obtained with catalytic oxidation [17]. However, catalytic oxidation requires high temperature ($800\text{--}850\ ^\circ\text{C}$), high pressure, metal oxides such as Cr_2O_3 , CuO or V_2O_5 and metal (Pt or Pd) as a catalyst. Catalytic oxidation is therefore more expensive than electroperoxidation.

Faecal coliform abatement depended on the current intensity (Figure 7). At low intensity (0.5 A), 1 log was removed while at high intensity (2 A), 3 log were removed. High intensity induced larger peroxide and free radical concentrations. This is in conformity with established relationships between hydrogen peroxide concentration and disinfection [18, 19]. However is the disinfection induced by electroperoxidation comparable to disinfection with hydrogen peroxide alone?

Noncarbonated natural mineral water was electrolysed in unit 1, without a catalyst, to reach a $12\ \text{mg l}^{-1}$ plateau in the concentration of peroxide. Then a sample was taken from the tank, poured in a beaker containing a brass grid and contaminated with *Pseudomonas aeruginosa*. This sample was therefore treated only with hydrogen peroxide and free radicals. The remaining tank content was also contaminated while the electrolysis was maintained in operation in presence of the catalyst; this second sample was therefore subjected to two processes, that is, the chemical effect of peroxide and free radicals and the electrical effect. Disinfection was much more effective with simultaneous electrolysis, which induced more than 3 log difference (Figure 8). Bacterial cells are protected by a membrane constituted of a bimolecular layer of phospholipids with hydrophobic and hydrophilic parts [19]. Protein inclusions within the membrane allow ion exchange with the cell's

environment. Many attempts have been made to kill microorganisms using electrochemical processes. Okochi et al. [20] reported killing bacteria by direct electron transfer between an electrode and the cell. Furthermore, the potential difference between the two electrodes of the electroperoxidation reactor involved an electrical field, which can have disinfectant effects [21, 22].

The phospholipid membrane is not easily oxidised, whereas the proteins are easily destroyed by direct anodic oxidation at the electrode surface [23]. The cell cannot then exchange ions. However it could be re-activated in a more favourable environment [24]. Its total destruction requires an oxidant being able to cross the membrane and reach its vital centres, that is, hydrogen peroxide generated at the cathode [25]. Moreover electrolysis induces a pH gradient that affects bacteria [26, 27].

Another interesting peculiarity of hydrogen peroxide results from its residual effect. The effluent of a municipal sewage plant was electrolysed in unit 1, for 3 h at a 1.5 A intensity. Then the current was switched off and bacteria and hydrogen peroxide concentrations were monitored. The bacterial concentration rapidly decreased towards a plateau (Figure 9), while

the peroxide concentration remained high after 90 h (Figure 10). Hydrogen peroxide prevents bacterial growth in water [15]. It provides a residual disinfecting ability contrary to other oxidation processes such as ozonisation and ultraviolet light [12].

4. Conclusions

- (i) Hydrogen peroxide was electrochemically generated at a high rate with a two-electrode cell and without chemical additions.
- (ii) The faradaic yield was low, about 0.21.
- (iii) Electroperoxidation was effective in removing turbidity and dissolved organic carbon.
- (iv) Disinfection by electroperoxidation combines the direct effect of electrolysis with the oxidative indirect effect of hydrogen peroxide.
- (v) Electroperoxidation could be the basis of a process for water disinfection for various applications such as supply of drinking water, tertiary treatment of wastewater and swimming pool use, but

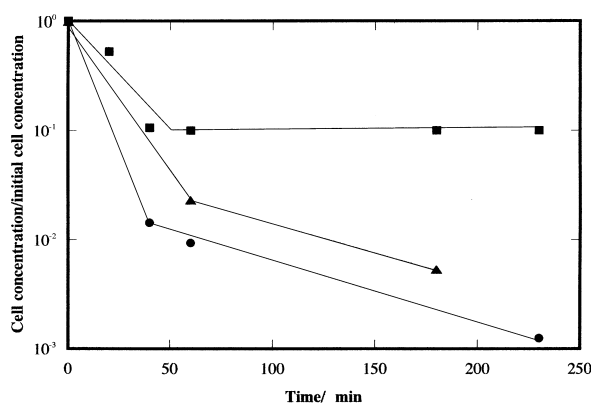


Fig. 7. Removal of faecal coliforms at different intensities (effluent of Mèze sewage plant, 80 mg l⁻¹ COD). Key: (■) 0.5 A; (▲) 1.5 A; (●) 2 A.

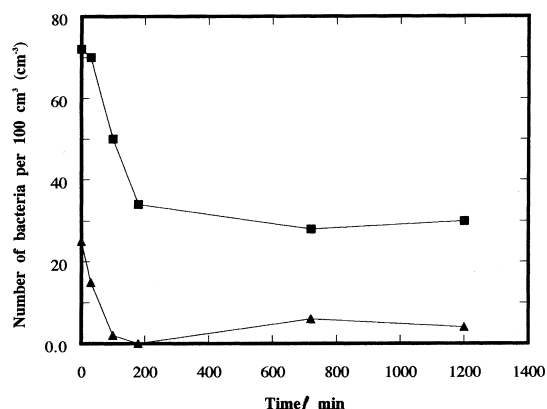


Fig. 9. Number of cells per 100 ml against elapsed time (effluent of the Mèze sewage plant, 23 mg l⁻¹ initial COD). Key: (■) faecal coliforms; (▲) pseudomonas.

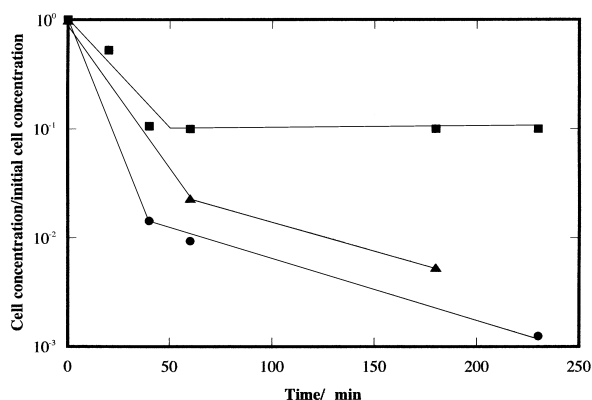


Fig. 8. Compared survival of *Pseudomonas aeruginosa* with electrolysis and chemical oxidation (noncarbonated natural mineral water, initial concentration of 20 000 cells ml⁻¹). Key: (■) electrolysis; (▲) chemical treatment; (●) no treatment.

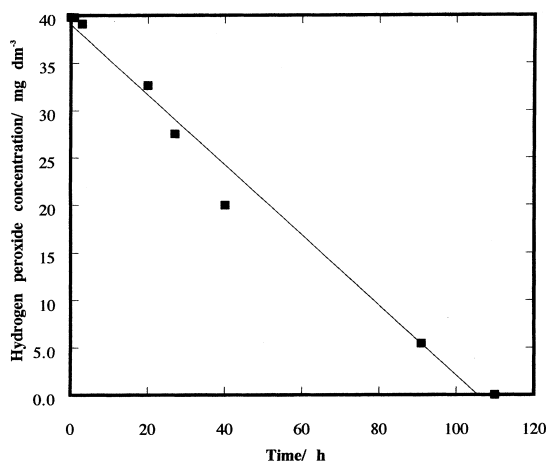


Fig. 10. Residual hydrogen peroxide concentration against elapsed time (effluent of the Mèze sewage plant, 23 mg l⁻¹ initial COD).

consequences of anode fouling or degradation must be further investigated.

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